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(54) **Recording material**

(57) A recording material contains both a microcapsule containing an electron-donating color former dissolved in a solvent and an electron-accepting developer. The electron-donating color former comprises Crystal Violet Lactone, and the solvent comprises a mixture of a

vegetable oil which has a fatty acid residue composition containing an oleic acid residue in the range of 10 to 60 weight % and a specific bisphenol compound, the bisphenol compound being contained in the mixture in an amount of 2 to 40 weight parts based on 100 weight parts of the vegetable oil.

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Description**FIELD OF THE INVENTION**

5 The present invention relates to a recording material which is employable for a pressure sensitive material and a heat sensitive material.

BACKGROUND OF THE INVENTION

10 Recording materials that contain both a micro capsule containing an electron-donating color former (hereinafter may be referred to as "color former") dissolved in a solvent and an electron-accepting developer (hereinafter may be referred to as "developer"), are widely used. In the recording material, the color former reacts with the developer to form a colored image.

15 The recording materials are roughly classified into the two groups, namely, a pressure sensitive recording material and a heat sensitive recording material. The pressure sensitive recording material utilizes the mechanisms that the micro capsule containing the color former is ruptured by application of pressure to form a color image through the reaction of the color former with the developer. The pressure sensitive recording material includes a no-carbon-paper-type recording material that a color former layer comprising a micro capsule containing a color former (hereinafter may be referred to as "color former layer") and a developer layer containing an electron-accepting developer (hereinafter may be referred to as "developer layer") are respectively formed on surfaces of separate supports or separate surfaces of one support and are in contact with each other to be used; and a self-coloring-type pressure sensitive recording material (e.g., pressing-type paper or self-contained paper) comprising a self-coloring layer having both the color former and the developer provided on one side surface of a support.

25 The no-carbon-paper-type recording material consists of an upper paper having a color former layer provided on one side surface of a support (which usually is paper sheet), an intermediate paper having a color former layer provided on one side surface of a support and a developer layer on another side surface of the support, and a lower paper having a developer layer provided on one side surface of a support. The intermediate paper is usually used in the form of two or more sheets. Such a no-carbon-paper-type recording material is employed by bringing the color former into contact with the developer to form a colored image.

30 In the self-coloring-type pressure sensitive recording material, when pressure is applied to a surface having a self-coloring layer, a microcapsule in the layer is ruptured to form a color image on the self-coloring layer through the reaction of the color former with the developer. Therefore, the material is usually employed for writing or drawing an image such as an image of letters on a paper placed on the self-coloring layer with writing instruments or a typewriter, for directly printing a colored image on the self-coloring layer with a printer or a typewriter, or for printing a letter for OCR (optical character reader) on the self-coloring layer.

35 In preparation of plural copies, a self-coloring-type pressure sensitive recording material using an upper paper having a self-coloring layer provided on one side surface of a support and a color former layer on another side surface of the support, in combination with an intermediate paper having a color former layer and developer layer and a lower paper having a developer layer is occasionally employed. Types of the self-coloring layer of the self-coloring-type pressure sensitive recording material include a two layers-type consisting of a color former layer containing a microcapsule containing a color former and a developer layer containing a developer which are superposed upon each other, and a one layer-type consisting of one layer containing a color former and a developer.

45 The heat sensitive recording materials containing a microcapsule, for example, are those having a heat sensitive layer which contains a microcapsule containing a color former and a developer, as described in Japanese Patent Provisional Publications No. 63(1988)-265682 and No. 1(1989)-105782. Such a recording material has the advantages that can be designed for OHP (over head projector) or multicolor type.

50 The microcapsule, which is contained in the above recording materials, contains a color former dissolved in a solvent. It is needed that such a solvent can dissolve the color former. Examples of the solvents generally include kerosine, paraffin, naphthene oil, alkylated biphenyl, alkylated terphenyl, chlorinated paraffin, alkylated naphthalene, diaryl alkane and phthalic acid ester. However, these solvents generally give off malodor. Some of them are harmful to living things so that they are fraught with the danger that bring out environmental pollution (e.g., poor working condition). In more detail, when the recording material is prepared using the solvents or the recording material containing the solvents is used, the above problem occur.

55 Japanese Patent Provisional Publication No. 50 (1975)-90409 describes a process for preparation of a pressure sensitive recording paper comprising the steps of dissolving a color former in an animal or vegetable oil heated at 105 to 260°C to prepare a color former solution, and forming a microcapsule layer containing the color former solution on support.

The animal or vegetable oils used in the process are natural edible materials mainly composed of triglyceride. The

oils have no malodor and are safe from the viewpoint of ecology, and further are available at low prices. Therefore, the oils are suitable for solvents for the color former solution enclosed with the microcapsule.

However, the animal or vegetable oils generally do not have a sufficient dissolving power required for dissolving a color former and therefore it is difficult to increase a concentration of the color former in the resulting solution. In the process described in the Japanese Patent Provisional Publication No. 50(1975)-90409, a color former is dissolved in an animal or vegetable oil by heating the oil at a high temperature of 105 to 260°C. However, this heating brings about deterioration of quality of the oil due to oxidation, and the heated oil occasionally gives off malodor. Further, the oil itself occasionally inhibits coloring of the color former (i.e., desensitizes the color former).

The applicant has filed an application of a recording material using a glyceride such as vegetable oil wherein shows coloring of high density with the European Patent Office. The application has a publication number of EP 629511-A2. In more detail, the recording material has a microcapsule containing a particular fluoran compound (electron-donating color former) dissolved in a vegetable oil.

It has been desired, however, that color formers other than the above compound can be utilized in order to give various hues, and further desired that easily available color formers can be utilized in a large amount. For example, Crystal Violet Lactone, which is widely employed as a color former giving blue coloration, is not satisfactorily dissolved in a vegetable oil. When a color former solution that Crystal Violet Lactone is not sufficiently dissolved in a vegetable oil is encapsulated, a resultant microcapsule solution contains not only the microcapsule but also the color former which has not been encapsulated or a part of materials for forming a shell of the microcapsule which has not played a role in the formation of the shell. Therefore, a process of preparation of a recording material using the above color former solution is disadvantageous from the viewpoint of productivity, and the recording material using the microcapsule solution containing the parts of the color former or the materials cannot show coloring of high density.

SUMMARY OF THE INVENTION

It is an object of the present invention to provide a recording material which has no malodor and is safe from the viewpoint of ecology, and which shows coloring of high density.

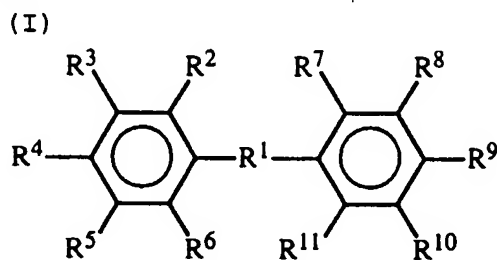
It is another object of the invention to provide a pressure sensitive recording material which has no malodor and is safe from the viewpoint of ecology, and which shows coloring of high density.

It is a further object of the invention to provide a heat sensitive recording material which has no malodor and is safe from the viewpoint of ecology, and which shows coloring of high density.

The present inventor has studied to find a solvent containing mainly a vegetable oil in which Crystal Violet Lactone (CLV) can be easily dissolved. In more detail, he has studied to find a specific compound which is added to the vegetable oil to enable Crystal Violet Lactone to dissolve in the vegetable oil containing the compound. As a result, he found the specific bisphenol compound having the following formula (I) as the compound capable of dissolving CLV in the vegetable oil.

The invention resides in a recording material which contains both a microcapsule containing an electron-donating color former dissolved in a solvent and an electron-accepting developer;

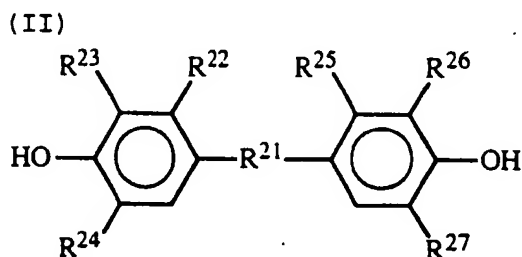
wherein the electron-donating color former comprises Crystal Violet Lactone, and the solvent comprises a mixture of a vegetable oil which has a fatty acid residue composition containing an oleic acid residue in an amount of 10 to 60 weight % and a bisphenol compound having the formula (I):



wherein R¹ represents -S-, -CR¹²R¹³, in which each of R¹² and R¹³ independently represents a hydrogen atom or an alkyl group of 1 to 6 carbon atoms, or -SO₂-; and each of R², R³, R⁴, R⁵, R⁶, R⁷, R⁸, R⁹, R¹⁰ or R¹¹ independently represents a hydrogen atom, an alkyl group of 1 to 8 carbon atoms or a hydroxyl group, provided that one or two groups of R², R³, R⁴, R⁵ and R⁶ and one or two groups of R⁷, R⁸, R⁹, R¹⁰ and R¹¹ represent a hydroxyl group; the bisphenol compound being contained in the mixture in an amount of 2 to 40 weight parts based on 100 weight parts of the vegetable oil.

Preferred embodiments of the recording material are as follows:

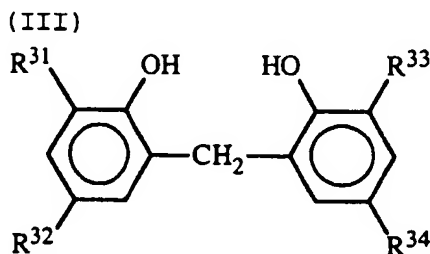
- (1) The recording material wherein R^2 and/or R^4 and R^7 and/or R^9 is a hydroxyl group.
 (2) The recording material wherein R^2 and R^7 or R^4 and R^9 are a hydroxyl group.
 (3) The recording material wherein the bisphenol compound has the formula (II):



wherein R^{21} represents -S-, $-CR^{28}R^{29}$ - in which each of R^{28} and R^{29} independently represents a hydrogen atom or an alkyl group of 1 to 6 carbon atoms, or $-SO_2-$; and each of R^{22} , R^{23} , R^{24} , R^{25} , R^{26} and R^{27} independently represents a hydrogen atom or an alkyl group of 1 to 8 carbon atoms;

or

the formula (III):



wherein each of R^{31} , R^{32} , R^{33} and R^{34} independently represents a hydrogen atom or an alkyl group of 1 to 8 carbon atoms.

- (4) The recording material wherein the bisphenol compound is contained in the mixture in an amount of 5 to 30 weight parts based on 100 weight parts of the vegetable oil.
 (5) The recording material wherein the vegetable oil is at least one selected from the group consisting of soybean oil, corn oil, rapeseed oil, cotton seed oil, sesame oil, peanut oil and sunflower oil.
 (6) The recording material wherein the developer comprises clay materials.
 (7) The recording material wherein Crystal Violet Lactone occupies not less than 50 weight % of the total amount of the electron-donating color former.
 (8) The recording material wherein the electron-donating color former further contains at least one selected from the group consisting of Benzoylleucomethylene Blue, fluoran compounds, indolylphthalide compounds and indolylazaphthalide compounds.
 (9) The recording material wherein the electron-donating color former is contained in an amount of 3 to 12 weight % in the solvent.
 (10) The recording material wherein the microcapsule has a shell of polyurethane/polyurea resin.

Further, the invention resides in a pressure sensitive recording material which contains both a pressure rupturable color former layer comprising a microcapsule which contains an electron-donating color former dissolved in a solvent and a developer layer comprising an electron-accepting developer;

wherein the electron-donating color former comprises Crystal Violet Lactone, and the solvent comprises a mixture of a vegetable oil which has a fatty acid residue composition containing an oleic acid residue in an amount of 10 to 60 weight % and a bisphenol compound having the above formula (I), the bisphenol compound being contained in the mixture in an amount of 2 to 40 weight parts based on 100 weight parts of the vegetable oil.

Furthermore, the invention resides in a pressure sensitive recording material which comprises an upper paper comprising a paper sheet and a pressure rupturable color former layer provided on the paper sheet, and a lower paper comprising a paper sheet and a developer layer provided on the paper sheet, said color former layer comprising a microcapsule which contains an electron-donating color former dissolved in a solvent and said developer layer comprising an electron-accepting developer;

wherein the electron-donating color former comprises Crystal Violet Lactone, and the solvent comprises a mixture

of a vegetable oil which has a fatty acid residue composition containing an oleic acid residue in an amount of 10 to 60 weight % and a bisphenol compound having the above formula (I), the bisphenol compound being contained in the mixture in an amount of 2 to 40 weight parts based on 100 weight parts of the vegetable oil.

Preferred embodiment of the above pressure sensitive recording material are as follows:

(1) The pressure sensitive recording material which further has at least one intermediate paper which has a paper sheet, a color former layer provided on one side surface of the paper sheet and a developer layer on another side surface of the paper sheet between the upper paper and the lower paper.

The recording material of the invention employs the vegetable oil containing the specific bisphenol compound as a solvent for dissolving Crystal Violet Lactone (CVL). In more detail, although CVL scarcely dissolves in a vegetable oil, addition of the bisphenol compound in a small amount to the vegetable oil enables CVL to dissolve in the vegetable oil. The recording material obtained by using the vegetable oil containing the specific bisphenol compound shows coloring of high density because CVL is satisfactorily dissolved in the solvent. Hence, the recording material of the invention is one that is safe from the viewpoint of ecology and shows coloring of high density. Particularly, it is useful for a pressure sensitive recording material.

Furthermore, the solvent generally give off no malodor and are mostly not harmful to living things. Therefore, use of the solvent do not bring out poor working condition, and naturally do not environmental pollution.

BRIEF DESCRIPTION OF DRAWINGS

Fig. 1 is a schematic sectional view of a typical structure of the no-carbon-paper-type pressure sensitive recording material according to the invention.

Fig. 2 is a schematic sectional view of a typical structure of the self-coloring-type pressure sensitive recording material according to the invention.

Fig. 3 is a schematic sectional view of another structure of the self-coloring-type pressure sensitive recording material according to the invention.

DETAILED DESCRIPTION OF THE INVENTION

The recording material of the invention contains both a microcapsule containing an electron-donating color former dissolved in a solvent and an electron-accepting developer. The recording material is not restricted in its form so long as it contains a microcapsule containing a color former dissolved in a solvent.

The typical structures of the recording materials of the invention are described below.

Fig. 1 shows a typical structure of the no-carbon-paper-type pressure sensitive recording material. A upper paper 1 has a color former layer 3 provided on one side surface of a support 2. An intermediate paper 4 has a developer layer 5 provided on one side surface of a support 6 and a color former layer 7 on another side surface of the support 6. A lower paper 8 has a developer layer 9 provided on one side surface of a support 10. The three paper are superposed in the order as shown in Fig. 1. Although the intermediate paper 4 is usually used in the form of a pile of two or more sheets, it may be not used. Recording (formation of image) is generally performed by applying pressure to the opposite surface of the color former layer 3 of the support 2 to bring the color former into contact with the developer.

Fig. 2 shows a typical structure of the self-coloring-type pressure sensitive recording material. Both a color former layer 11 and a developer layer 12 are provided on one side surface of a support 13.

Fig. 3 shows another structure of the self-coloring-type pressure sensitive recording material. A self-coloring layer 14 containing both a color former and a developer is provided on one side surface of a support 13.

The heat sensitive recording material has the same structure as that shown in Fig. 3. The self-coloring layer 14 corresponds to a heat sensitive layer.

The recording material of the invention is characterized by the use of the vegetable oil containing the specific bisphenol compound as the solvent for dissolving Crystal Violet Lactone (color former) contained in the microcapsule. As for an example of the no-carbon-paper-type pressure sensitive material, a detailed explanation is given below. It will be easily understood that the similar effect is obtained in recording materials having other forms.

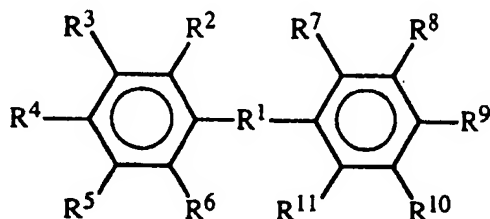
In the invention, a solvent used for dissolving the color former comprises a mixture of a vegetable oil which has a fatty acid residue composition containing an oleic acid residue in an amount of 10 to 60 weight % and a bisphenol compound having the above formula (I). The bisphenol compound is contained in the mixture in an amount of 2 to 40 weight parts based on 100 weight parts of the vegetable oil.

Examples of the vegetable oil having the fatty acid residue composition include soybean oil (oleic acid residue content in the oil [OARC] = 20 to 35 weight %), corn oil ([OARC] = 25 to 45 weight %), rapeseed oil ([OARC] = 10 to 35 weight %), cotton seed oil ([OARC] = 15 to 30 weight %), sesame oil ([OARC] = 35 to 46 weight %), peanut oil

5 ([OARC] = 35 to 60 weight %) and sunflower oil ([OARC] = 15 to 35 weight %). Preferred vegetable oils are soybean oil, corn oil, rapeseed oil and cotton seed oil, because these oils have a relatively strong dissolving power for dissolving the color former, and are apt to show coloring of high density by reacting with the developer, and further are easily available as industrial products. These oils are employable singly or in combination. In contrast, olive oil ([OARC] = 70 to 85 weight %), which has a fatty acid residue composition containing an oleic acid residue in an amount of more than 60 weight %, is not preferred because of low dissolving power for dissolving the color former.

The solvent of the invention used for dissolving the color former comprises the vegetable oil containing the bisphenol compound having the formula (I).

(I)

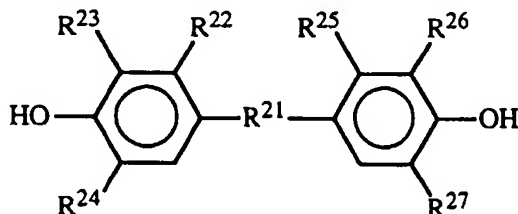


20 wherein R^1 represents -S-, $-CR^{12}R^{13}$, in which each of R^{12} and R^{13} independently represents a hydrogen atom or an alkyl group of 1 to 6 carbon atoms, or $-SO_2$; and each of R^2 , R^3 , R^4 , R^5 , R^6 , R^7 , R^8 , R^9 , R^{10} or R^{11} independently represents a hydrogen atom, an alkyl group of 1 to 8 carbon atoms or a hydroxyl group, provided that one or two groups of R^2 , R^3 , R^4 , R^5 and R^6 and one or two groups of R^7 , R^8 , R^9 , R^{10} and R^{11} represent a hydroxyl group.

25 R^1 preferably is -S-, $-CR^{12}R^{13}$, in which each of R^{12} and R^{13} independently represents a hydrogen atom or an alkyl group of 1 to 4 carbon atoms (e.g., methylene, ethylidene, propylidene, isopropylidene or butylidene), or $-SO_2$; and especially -S-, $-SO_2$, a methylene group, an isopropylidene group or a butylidene group. Each of R^2 , R^3 , R^4 , R^5 , R^6 , R^7 , R^8 , R^9 , R^{10} or R^{11} preferably is a hydrogen atom, an alkyl group of 1 to 4 carbon atoms (e.g., methyl, ethyl, propyl, isopropyl, n-butyl or t-butyl) or a hydroxyl group; and especially a hydrogen atom, a methyl group, an ethyl group, a t-butyl group or a hydroxyl group. Of these groups (R^2 to R^{11}), at least one groups of R^2 and R^4 and at least one groups of R^7 and R^9 preferably are a hydroxyl group, and especially R^2 and R^7 or R^4 and R^9 preferably are a hydroxyl group.

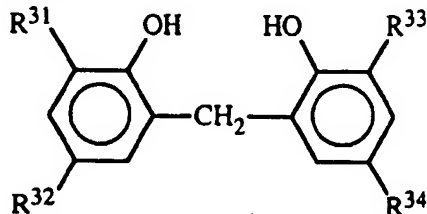
Further, the bisphenol compound of the formula (I) preferably is a compound of the formula (II):

(II)



45 wherein R^{21} represents -S-, $-CR^{28}R^{29}$, in which each of R^{28} and R^{29} independently represents a hydrogen atom or an alkyl group of 1 to 6 carbon atoms, or $-SO_2$; and each of R^{22} , R^{23} , R^{24} , R^{25} , R^{26} and R^{27} independently represents a hydrogen atom or an alkyl group of 1 to 8 carbon atoms;
or
the formula (III):

(III)



wherein each of R^{31} , R^{32} , R^{33} and R^{34} independently represents a hydrogen atom or an alkyl group of 1 to 8 carbon

atoms.

In the formula (II), R^{21} preferably is $-S-$, $-CR^{28}R^{29}$, in which each of R^{28} and R^{29} independently represents a hydrogen atom or an alkyl group of 1 to 4 carbon atoms (e.g., methylene, ethylidene, propylidene, isopropylidene or butylidene), or $-SO_2-$; and especially $-S-$, $-SO_2-$, a methylene group, an isopropylidene group or a butylidene group.

Each of R^{22} , R^{23} , R^{24} , R^{25} , R^{26} and R^{27} preferably is a hydrogen atom or an alkyl group of 1 to 4 carbon atoms (e.g., methyl, ethyl, propyl, isopropyl, n-butyl or t-butyl); and especially a hydrogen atom, an ethyl group or a t-butyl group.

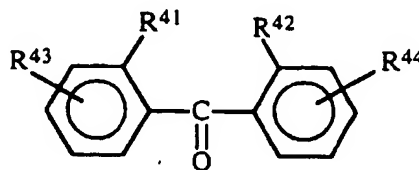
In the formula (III), each of R^{31} , R^{32} , R^{33} and R^{34} preferably is a hydrogen atom or an alkyl group of 1 to 4 carbon atoms (e.g., methyl, ethyl, propyl, isopropyl, n-butyl or t-butyl); and especially a hydrogen atom, an ethyl group or a t-butyl group.

Preferred examples of bisphenol compounds having the above formula (I) (formula (II) or (III)) include 4,4'-methylenediphenol, 4,4'-isopropylidenediphenol, 4,4'-butylidenediphenol, 4,4'-methylenebis(3-methyl-6-t-butylphenol), 4,4'-butylidenebis(3-methyl-6-t-butylphenol), 4,4'-methylenebis(2,6-di-t-butylphenol), bis(4-hydroxyphenyl)sulfone, bis(3,5-dimethyl-4-hydroxyphenyl)sulfone, 4,4'-thiobis(3-methyl-6-t-butylphenol), 2,2'-methylenebis(4-methyl-6-t-butylphenol) and 2,2'-methylenebis(4-ethyl-6-t-butylphenol).

In the invention, a solvent for dissolving the coloring former such as Crystal Violet Lactone is a mixture consisting of the vegetable oil and the bisphenol compound of the formula (I) in 2 to 40 parts based on 100 weight parts of the vegetable oil. The content of the bisphenol compound preferably is in the range of 5 to 40 parts, especially in the range of 5 to 30 parts. When the bisphenol compound is contained in an amount of more than 40 parts, a microcapsule dispersing solution (coating solution for forming a coloring former layer) is colored. This is considered because a hydroxyl group of the bisphenol compound serves as a developer. In the case that such a microcapsule dispersing solution is coated on a paper sheet, the resultant paper shows a lowered whiteness degree. Further, the use of more than 40 parts difficultly provides a recording material which has no malodor and safety from the viewpoint of ecology. When the bisphenol compound is contained in an amount of less than 2 parts, Crystal Violet Lactone cannot be used in an

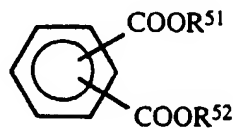
In the invention, a conventional solvent mentioned previously is employable in the amount that the resultant recording material does not give off malodor (not more than 30 weight % per vegetable oil), in combination of the vegetable oil and the bisphenol compound.

The following compounds (i.e., a benzophenon compound of the formula (IV), or an aromatic carboxylic acid ester compound of the formula (V) or (VI)) are employable in combination of the vegetable oil and the bisphenol compound.

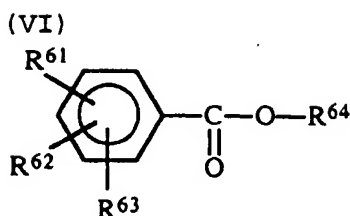


In the formula (IV), each of R^{41} and R^{42} independently represents a hydrogen atom, a hydroxyl group, an alkoxy group of 1 to 12 carbon atoms, a carboxyl group or an alkoxy carbonyl group of 2 to 12 carbon atoms; and each of R^{43} and R^{44} independently represents a hydrogen atom, a hydroxyl group, an alkyl group of 1 to 12 carbon atoms, a carboxyl group, an alkoxy group of 1 to 18 carbon atoms or an aryloxy group of 6 to 10 carbon atoms (e.g., phenoxy).

(V)



In the formula (V), R^{51} represents an alkyl group of 2 to 12 carbon atoms, a cycloalkyl group of 5 to 8 carbon atoms, a hydroxyl group, an aryl group of 6 to 10 carbon atoms, an aralkyl group of 7 to 10 carbon atoms or $-CH_2COOR^{53}$ in which R^{53} represents alkyl of 1 to 12 carbon atoms or phenyl; and R^{52} represents an alkyl group of 6 to 12 carbon atoms, a cycloalkyl group of 5 to 8 carbon atoms, a hydroxyl group, an aryl group of 6 to 10 carbon atoms, an aralkyl group of 7 to 10 carbon atoms or $-CH_2COOR^{53}$ in which R^{53} represents alkyl of 1 to 12 carbon atoms or phenyl.



In the formula (VI), each of R⁶¹, R⁶² and R⁶³ independently represents a hydrogen atom, a hydroxyl group, an alkoxy group of 1 to 12 carbon atoms, an alkyl group of 1 to 12 carbon atoms or an aralkyl group of 7 to 18 carbon atoms; and R⁶⁴ represents an alkyl group of 6 to 12 carbon atoms, an aryl group of 6 to 10 carbon atoms (e.g., phenyl), an aralkyl group of 7 to 10 carbon atoms, an alkylaryl group of 7 to 18 carbon atoms or an alkoxyaryl group of 7 to 18 carbon atoms.

In the invention, known color formers can be employed together with Crystal Violet Lactone for purpose of controlling tone. Examples of the known color formers include triphenylmethanephthalide compounds other than Crystal Violet Lactone, Benzoylleucomethylene Blue, fluoran compounds, phenothiazine compounds, indolylphthalide compounds, indolylazaphthalide compounds, leucoauramine compounds, rhodaminelactam compounds, triphenylmethane compounds, triazene compounds and spiropyran compounds. Preferred are Benzoylleucomethylene Blue, fluoran compounds, indolylphthalide compounds and indolylazaphthalide compounds.

In the invention, Crystal Violet Lactone is generally used in an amount of not less than 50 weight % based on the total amount of the used color formers, preferably 60 to 100 weight %, and especially 80 to 100 weight %.

The microcapsule containing the color former is prepared by dissolving the color former in a mixture (solvent) of the vegetable oil and the bisphenol compound of the formula (I). The color former is preferably dissolved in the solvent at a temperature of 80 to 130°C. In the case of a temperature lower than 80°C, the color former is not easily dissolved in the solvent. In the case of a temperature higher than 130°C, the vegetable oil is occasionally deteriorated. The color former is generally contained in the solution of the color former in an amount of 3 to 12 % by weight based on an amount of the solvent, especially 3 to 10 weight %.

The microcapsule of the invention containing the color former dissolved in the solvent is prepared according to the known method such as an interfacial polymerization method, an internal polymerization method, a phase separation method, an external polymerization method or a coarservation method.

As the shell material of the microcapsule, waterinsoluble or oil-insoluble polymers which is used in the conventional pressure sensitive material are employable. Examples of the shell material include polyurethane/polyurea resin, melamine/formaldehyde resin and gelatin. The shell material is preferred to be polyurethane/polyurea resin having high resistance to heat-fogging. The microcapsule dispersion for forming the shell of polyurethane/polyurea resin to incorporate the color former, is prepared by, for example, the steps of dissolving a multi-functional isocyanate compound and a multi-functional hydroxyl compound (further UV absorbent if desired) in the solution prepared by dissolving the color former in the solvent as above, dispersing the resultant solution to a hydrophilic liquid, adding a multi-functional amine to the resultant dispersing solution, and coating the polyurethane/polyurea resin around a drop of the solution. The multi-functional hydroxyl compound and the multi-functional amine may be used in combination as above, or either of them may be used.

Examples of the multi-functional isocyanate compounds include an isocyanurate body of hydrogenated xylene diisocyanate (hydrogenated XDI), an isocyanurate body of isophorone diisocyanate (hydrogenated IPDI), diphenylmethane-4,4'-diisocyanate, a hexamethylene diisocyanate adduct of methylolpropane, a biuret body of hexamethylene diisocyanate, an isocyanurate body of hexamethylene diisocyanate, polymethylenepolyphenyl isocyanate, carbodiimide-modified diphenylmethane diisocyanate, a tolylene diisocyanate adduct of methylolpropane, a xylene diisocyanate adduct of methylolpropane, an isocyanurate body of tolylene diisocyanate, a hydrogenated xylene diisocyanate adduct of methylolpropane, an isophorone diisocyanate adduct of methylolpropane, a biuret body of xylene diisocyanate and tris(p-isocyanatophenyl)thiophosphite.

Preferred are an isocyanurate body of hydrogenated xylene diisocyanate and an isocyanurate of isophorone diisocyanate because they dissolve satisfactorily in the vegetable oil. As the multi-functional isocyanate compounds, a mixture of at least one of the isocyanurate bodies and an aromatic multi-functional isocyanate is preferably employed. A ratio of the isocyanurate and the aromatic isocyanate is preferably in the range of 8:2 to 2:8, especially 7:3 to 3:7, by weight (isocyanurate:aromatic isocyanate).

Examples of the multi-functional hydroxyl compound which reacts (or polymerizes) with the multi-functional isocyanate compound, include water, multi-functional hydroxyl compounds and multi-functional amines. Examples of the multi-functional hydroxyl compounds include aliphatic or aromatic multi-functional alcohols, polyester having hydroxy, polyalkylene ether having hydroxy and an alkylene oxide adduct of multi-functional amine.

The multi-functional amines generally are compounds which have two or more -NH- or -NH₂ groups in each mo-

lecular and are soluble in hydrophilic liquid. Examples of the amines include ethylenediamine, diethylenetriamine, triethylenetetramine, tetraethylenepentamine, 1,3-propylenediamine, hexamethylenediamine, phenylenediamine, diamionaphthalene and xylylenediamine.

The dispersing solution of the microcapsule prepared above is directly employed as a coating solution for forming the color former layer. Otherwise, the coating solution is prepared by adding further a binder and/or an agent for protecting a capsule to the dispersing solution. The resultant coating solution is coated on the support according to a known coating method and the coated layer is dried. Thus, the color former layer for the no-carbon-paper-type pressure sensitive recording material is formed. Examples of the binder include a water-soluble binder and a latex binder and examples of the agent for protecting a capsule include powders of cellulose, powders of starch and talc.

As materials of the support, materials employed for the support of the conventional pressure sensitive recording material and the conventional heat sensitive recording material. Examples of the materials of the support include a paper made of pulp, a surface treated paper, a synthetic paper made of plastic and a plastic film.

The coated amount of the color former layer formed on the support after drying generally is in the range of 0.05 to 0.30 g/m², and preferably is in the range of 0.08 to 0.20 g/m².

Examples of the developer contained in the developer layer of the no-carbon-paper-type pressure sensitive recording material include clay materials such as acid clay, activated clay, attapulgite, zeolite, bentonite and kaolin, metal salts of aromatic carboxylic acids (e.g., salicylic acid derivatives), and a phenol formaldehyde resin. The developer preferably is clay materials from the viewpoint of ecology.

A coating solution for forming the above developer layer is prepared according a known method. For example, the coating solution may further contain a binder. Examples of the binder include natural or synthetic polymers such as styrene/butadiene copolymer latex, polyvinyl acetate latex, polyacrylate latex, polyvinyl alcohol, polyacrylic acid, maleic anhydride/styrene copolymer, starch, casein, gelatin, gum arabic, carboxymethyl cellulose and methyl cellulose. The developer layer is formed on the support utilizing a known coating method.

The coated amount of the developer layer formed on the support after drying generally is in the range of 0.1 to 4.0 g/m², and preferably is in the range of 0.2 to 3.0 g/m².

The no-carbon-paper-type pressure sensitive recording material according to the invention has a composition similar to a conventional one except for employing the mixture of the vegetable oil and the specific bisphenol compound as the solvent for dissolving the color former.

Therefore, the no-carbon-paper-type pressure sensitive material of the invention can be prepared utilizing the known process.

As for other recording materials such as the self-coloring-type pressure sensitive recording material and the heat sensitive recording material described previously, they have a composition similar to conventional one except for employing the mixture of the vegetable oil and the specific bisphenol compound as the solvent for dissolving the color former. Therefore, the recording materials can be prepared utilizing the known processes.

The present invention is further described by the following examples.

EXAMPLE 1

(Preparation of coating solution for forming color former layer)

In a mixture (solvent) of 18.0 g of 4,4'-thiobis(3-methyl-6-*t*-butylphenol) and 100 g of rapeseed oil, 9.0 g of Crystal Violet Lactone as a color former was dissolved by heating at 120°C. Thus, a color former solution was prepared. In the resultant oily solution, a solution obtained by dissolving 6.0 g of an isocyanurate body of hydrogenated xylylene diisocyanate (Takenate D-127N, available from Takeda Chemical Industries, Ltd.; 75 weight % ethyl acetate solution) and 6.0 g of a carbodiimide-modified diphenylmethanediisocyanate (Cosmonate LK, available from Mitsui Toatsu Chemicals, Inc.; 100% solid content) as a multi-functional isocyanate compound in 30 g of ethyl acetate, and 3.0 g of butylene oxide adduct of ethylenediamine (adduct molar number of butylene oxide to ethylenediamine: 16.8 moles; Molecular weight: 1,267) as an alkylene oxide adduct of amine were dissolved to prepare a primary solution.

Subsequently, 10 g of polyvinyl alcohol and 5 g of carboxymethylcellulose were dissolved in 140 g of water placed in a stainless steel vessel to prepare a secondary solution. The primary solution was poured into the secondary solution while the secondary solution was vigorously stirred. Thus oil-in-water emulsion was formed. When a size of the oil droplet of the emulsion became 6.0 μm, the stirring power was weakened and then 100 g of water of 20°C was added to the emulsion. Subsequently, the temperature of the emulsion was gradually raised to 80°C and this temperature was kept for 90 minutes. Thus a capsule dispersing solution was obtained.

To the obtained capsule dispersing solution, 80 g of a polyvinyl alcohol 15 weight % solution, 15 g (solid content) of carboxy-modified SBR (styrene butadiene rubber) latex and 40 g of starch particles (mean particle size: 15 μm) were added, and further the solution was adjusted to 20 weight % by the addition of water to prepare a coating solution for forming a color former layer which contained a microcapsule containing a color former.

(Preparation of color former sheet)

On the one side of a paper of 50 g/m², the above coating solution for forming a color former layer was so coated as to have 4.0 g/m² in terms of solid content using an air-knife coater, and dried to prepare the color former sheet. This color former sheet scarcely gave off malodor. (Preparation of coating solution for forming developer layer)

To 100 g of water, 5 g of sodium hydroxide 20 weight % aqueous solution and 1 g of sodium hexametaphosphate 10 weight % aqueous solution were added to prepare a solution. To the solution, 2 g of magnesium oxide and 60 g of activated clay (Siltone F-242, available from Mizusawa Chemical Industry Co., Ltd.) were added and dispersed at 10,000 rpm for 5 minutes by means of a homogenizer (AM-7, available from Nippon Seiki Co., Ltd.) to prepare a developer dispersing solution.

In 100 g of sodium hydroxide aqueous solution (1 weight %), 5 g of wheat flour was dissolved to prepare a starch aqueous solution. To 100 g of the resultant dispersing solution, 35 g of the starch aqueous solution, 15 g (solid content) of a SBR (styrene butadiene rubber) latex and 4 g of additive were added and further the solution was adjusted to 20 weight % by the addition of water to prepare the coating solution for forming a developer layer. (Preparation of developer sheet)

On the one side of a paper of 50 g/m², the above coating solution for forming a developer layer was so coated as to have 5.0 g/m² in terms of solid content, using a bar coater, and dried to prepare the developer sheet.

EXAMPLE 2

(Preparation of color former sheet)

Procedures of Example 1 were repeated except for using the same amount of 2,2'-methylenebis(3-ethyl-6-t-butylphenol) instead of 4,4'-thiobis(3-methyl-6-t-butylphenol) to prepare a coating solution for forming a color former layer and then to prepare a color forming sheet. The resultant color former sheet scarcely gave off malodor. The developer sheet was also prepared in the same manner as in Example 1.

EXAMPLE 3

(Preparation of color former sheet)

Procedures of Example 1 were repeated except for using the same amount of corn oil instead of rapeseed oil to prepare a coating solution for forming a color former layer and then to prepare a color forming sheet. The resultant color former sheet scarcely gave off malodor. The developer sheet was also prepared in the same manner as in Example 1.

EXAMPLE 4

(Preparation of color former sheet)

Procedures of Example 1 were repeated except for using the same amount of soybean oil instead of rapeseed oil to prepare the coating solution for forming a color former layer and then to prepare a color forming sheet. The resultant color former sheet scarcely gave off malodor. The developer sheet was also prepared in the same manner as in Example 1.

EXAMPLE 5

(Preparation of color former sheet)

Procedures of Example 1 were repeated except for using 9.0 g of 4,4'-thiobis(3-methyl-6-t-butylphenol) and 9.0 g of 2-hydroxyl-4-methoxybenzophenone instead of 4,4'-thiobis(3-methyl-6-t-butylphenol) to prepare a coating solution for forming a color former layer and then to prepare a color forming sheet. The resultant color former sheet scarcely gave off malodor. The developer sheet was also prepared in the same manner as in Example 1.

EXAMPLE 6

(Preparation of color former sheet)

- 5 Procedures of Example 1 were repeated except for using 12.0 g of 4,4'-thiobis(3-methyl-6-t-butylphenol) and 6.0 g of dicyclohexyl phthalate instead of 4,4'-thiobis(3-methyl-6-t-butylphenol) to prepare a coating solution for forming a color former layer and then to prepare a color forming sheet. The resultant color former sheet scarcely gave off malodor. The developer sheet was also prepared in the same manner as in Example 1.

EXAMPLE 7

(Preparation of color former sheet)

- 15 Procedures of Example 1 were repeated except for using 9.0 g of 4,4'-thiobis(3-methyl-6-t-butylphenol), 6.0 g of 2-hydroxyl-4-methoxybenzophenone and 6.0 g of dicyclohexyl phthalate instead of 4,4'-thiobis(3-methyl-6-t-butylphenol) to prepare a coating solution for forming a color former layer and then to prepare a color forming sheet. The resultant color former sheet scarcely gave off malodor. The developer sheet was also prepared in the same manner as in Example 1.

COMPARISON EXAMPLE 1

(Preparation of color former sheet)

- 25 Procedures of Example 1 were repeated except for using 118.0 g of rapeseed oil instead of the mixture of rapeseed oil and 4,4'-thiobis(3-methyl-6-t-butylphenol) to prepare a coating solution for forming a color former layer and then to prepare a color forming sheet. The developer sheet was also prepared in the same manner as in Example 1.

COMPARISON EXAMPLE 2

(Preparation of color former sheet)

- 35 Procedures of Example 1 were repeated except for using 118.0 g of corn oil instead of the mixture of rapeseed oil and 4,4'-thiobis(3-methyl-6-t-butylphenol) to prepare a coating solution for forming a color former layer and then to prepare a color forming sheet. The developer sheet was also prepared in the same manner as in Example 1.

COMPARISON EXAMPLE 3

(Preparation of color former sheet)

- 40 Procedures of Example 1 were repeated except for using 118.0 g of soybean oil instead of the mixture of rapeseed oil and 4,4'-thiobis(3-methyl-6-t-butylphenol) to prepare a coating solution for forming a color former layer and then to prepare a color forming sheet. The developer sheet was also prepared in the same manner as in Example 1.

EVALUATION

- 45 (1) As for the color former solutions and capsule dispersing solutions (coating solution for forming color former layer) obtained in Examples and Comparison Examples, the following tests were performed.

a) Stability of color former solution

- 50 The color former solution obtained by dissolving the color former in the solvent was gradually cooled to a temperature of 50°C, and immediately occurrence of deposit (precipitate) was visually observed.

b) Residue produced in capsule dispersing solution

- 55 The resultant capsule dispersing solution (1,000 g) was filtered through a 250-mesh sieve, and the residue remained on the sieve was dried at 100°C for 1 hour to measure its weight.

(2) Using the color former sheet and the developer sheet, the evaluation of the developed color density was performed in the following manner.

c) Evaluation of developed color density

The color former sheet was placed on the developer sheet that the color former layer and the developer layer came into contact each other to form a composite. "m" of alphabet was typed on the composite using an electronic typewriter (IBM6747) to form a developed image ("m") on the developer layer. After the image of the developer layer was allowed to stand at room temperature for 24 hours, its density (D) was measured using Machbeth reflective densitometer.

The result is set forth in Table 1.

Table 1

	a) Stability of color former	b) Residue of capsule solution	c) Color density (D)
Example 1	None	5.5	0.57
Example 2	None	7.5	0.56
Example 3	None	5.6	0.56
Example 4	None	5.2	0.57
Example 5	None	5.8	0.57
Example 6	None	6.4	0.56
Example 7	None	6.2	0.56
Comp. Ex. 1	Observed	398.2	0.50
Comp. Ex. 2	Observed	389.3	0.50
Comp. Ex. 3	Observed	386.7	0.51

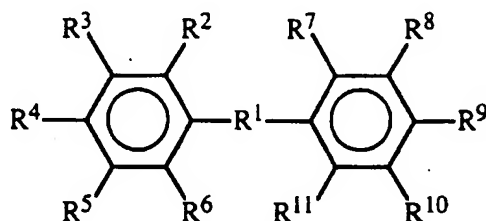
Any color former solutions prepared in Examples 1 to 7 showed excellent stability that there is not occurrence of deposit under the condition of a low temperature. Further, the capsule dispersing solutions prepared from the color former solutions scarcely produced residue. In contrast, the color former solutions prepared in Comparison Examples 1 to 3 which are used only the vegetable oil as a solvent showed occurrence of deposit at a low temperature, and the capsule dispersing solutions prepared from the color former solutions produced an amount of residue.

Furthermore, the recording materials obtained in Examples 1 to 7 showed the color images of high color densities with combination of the developer sheets. In contrast, the recording materials of Comparison Examples 1 to 3 did not show the color images of satisfactory color densities

Claims

1. A recording material which contains both a microcapsule containing an electron-donating color former dissolved in a solvent and an electron-accepting developer;
wherein the electron-donating color former comprises Crystal Violet Lactone, and the solvent comprises a mixture of a vegetable oil which has a fatty acid residue composition containing an oleic acid residue in an amount of 10 to 60 weight % and a bisphenol compound having the formula (I):

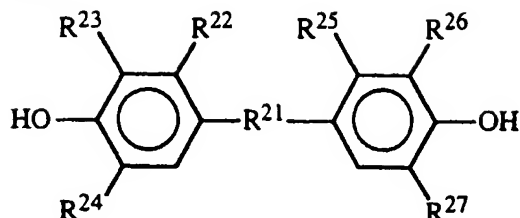
(I)



wherein R¹ represents -S-, -CR¹²R¹³- in which each of R¹² and R¹³ independently represents a hydrogen atom or an alkyl group of 1 to 6 carbon atoms, or -SO₂-; and each of R², R³, R⁴, R⁵, R⁶, R⁷, R⁸, R⁹, R¹⁰ or R¹¹ independently represents a hydrogen atom, an alkyl group of 1 to 8 carbon atoms or a hydroxyl group, provided that one or two groups of R², R³, R⁴, R⁵ and R⁶ and one or two groups of R⁷, R⁸, R⁹, R¹⁰ and R¹¹ represent a hydroxyl group; the bisphenol compound being contained in the mixture in an amount of 2 to 40 weight parts based on 100 weight parts of the vegetable oil.

2. The recording material as defined in claim 1, wherein the bisphenol compound has the formula (II):

(II)

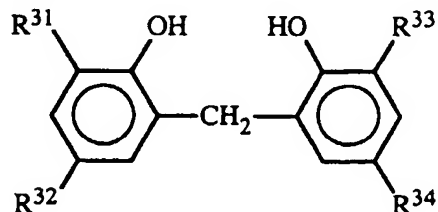


wherein R^{21} represents -S-, $-CR^{28}R^{29}-$ in which each of R^{28} and R^{29} independently represents a hydrogen atom or an alkyl group of 1 to 6 carbon atoms, or $-SO_2-$; and each of R^{22} , R^{23} , R^{24} , R^{25} , R^{26} and R^{27} independently represents a hydrogen atom or an alkyl group of 1 to 8 carbon atoms;

or

the formula (III):

(III)

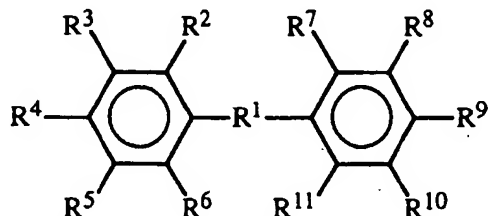


wherein each of R^{31} , R^{32} , R^{33} and R^{34} independently represents a hydrogen atom or an alkyl group of 1 to 8 carbon atoms.

3. The recording material as defined in claim 1, wherein the bisphenol compound is contained in the mixture in an amount of 5 to 30 weight parts based on 100 weight parts of the vegetable oil.
4. The recording material as defined in claim 1, wherein the vegetable oil is at least one selected from the group consisting of soybean oil, corn oil, rapeseed oil, cotton seed oil, sesame oil, peanut oil and sunflower oil.
5. The recording material as defined in claim 1, wherein the developer comprises clay materials.
6. A pressure sensitive recording material which has both a color former layer comprising a pressure rupturable microcapsule which contains an electron-donating color former dissolved in a solvent and a developer layer comprising an electron-accepting developer;

wherein the electron-donating color former comprises Crystal Violet Lactone, and the solvent comprises a mixture of a vegetable oil which has a fatty acid residue composition containing an oleic acid residue in an amount of 10 to 60 weight % and a bisphenol compound having the formula (I):

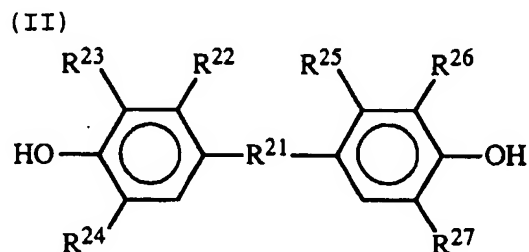
(I)



wherein R^1 represents -S-, $-CR^{12}R^{13}-$ in which each of R^{12} and R^{13} independently represents a hydrogen atom or an alkyl group of 1 to 6 carbon atoms, or $-SO_2-$; and each of R^2 , R^3 , R^4 , R^5 , R^6 , R^7 , R^8 , R^9 , R^{10} or R^{11} independently represents a hydrogen atom, an alkyl group of 1 to 8 carbon atoms or a hydroxyl group, provided that one or two groups of R^2 , R^3 , R^4 , R^5 and R^6 and one or two groups of R^7 , R^8 , R^9 , R^{10} and R^{11} represent a hydroxyl

group; the bisphenol compound being contained in the mixture in an amount of 2 to 40 weight parts based on 100 weight parts of the vegetable oil.

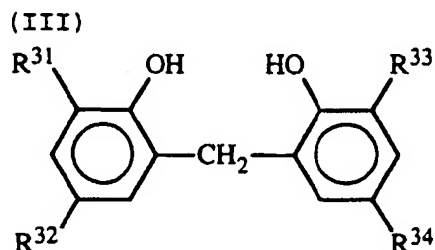
7. The pressure sensitive recording material as defined in claim 6, wherein the bisphenol compound has the formula (II):



wherein R^{21} represents $-S-$, $-CR^{28}R^{29}-$ in which each of R^{28} and R^{29} independently represents a hydrogen atom or an alkyl group of 1 to 6 carbon atoms, or $-SO_2-$; and each of R^{22} , R^{23} , R^{24} , R^{25} , R^{26} and R^{27} independently represents a hydrogen atom or an alkyl group of 1 to 8 carbon atoms;

or

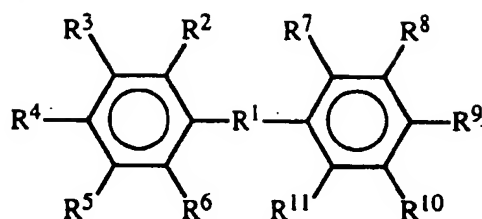
the formula (III):



wherein each of R^{31} , R^{32} , R^{33} and R^{34} independently represents a hydrogen atom or an alkyl group of 1 to 8 carbon atoms.

8. The pressure sensitive recording material as defined in claim 6, wherein the bisphenol compound is contained in the mixture in an amount of 5 to 30 weight parts based on 100 weight parts of the vegetable oil.
9. The pressure sensitive recording material as defined in claim 6, wherein the vegetable oil is at least one selected from the group consisting of soybean oil, corn oil, rapeseed oil, cotton seed oil, sesame oil, peanut oil and sunflower oil.
10. The pressure sensitive recording material as defined in claim 6, wherein the developer comprises clay materials.
11. A pressure sensitive recording material which comprises a upper paper comprising a paper sheet and a color former layer provided on the paper sheet, and a lower paper comprising a paper sheet and a developer layer provided on the paper sheet, said color former layer comprising a pressure rupturable microcapsule which contains an electron-donating color former dissolved in a solvent and said developer layer comprising an electron-accepting developer;
- wherein the electron-donating color former comprises Crystal Violet Lactone, and the solvent comprises a mixture of a vegetable oil which has a fatty acid residue composition containing an oleic acid residue in an amount of 10 to 60 weight % and a bisphenol compound having the formula (I):

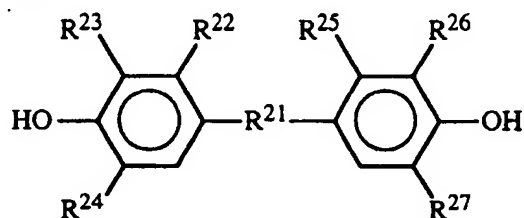
(I)



wherein R^1 represents $-S-$, $-CR^{12}R^{13}-$ in which each of R^{12} and R^{13} independently represents a hydrogen atom or an alkyl group of 1 to 6 carbon atoms, or $-SO_2-$; and each of R^2 , R^3 , R^4 , R^5 , R^6 , R^7 , R^8 , R^9 , R^{10} or R^{11} independently represents a hydrogen atom, an alkyl group of 1 to 8 carbon atoms or a hydroxyl group, provided that one or two groups of R^2 , R^3 , R^4 , R^5 and R^6 and one or two groups of R^7 , R^8 , R^9 , R^{10} and R^{11} represent a hydroxyl group; the bisphenol compound being contained in the mixture in an amount of 2 to 40 weight parts based on 100 weight parts of the vegetable oil.

12. The pressure sensitive recording material as defined in claim 11, wherein the bisphenol compound has the formula (II):

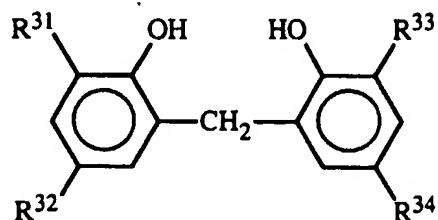
(II)



wherein R^{21} represents $-S-$, $-CR^{28}R^{29}-$ in which each of R^{28} and R^{29} independently represents a hydrogen atom or an alkyl group of 1 to 6 carbon atoms, or $-SO_2-$; and each of R^{22} , R^{23} , R^{24} , R^{25} , R^{26} and R^{27} independently represents a hydrogen atom or an alkyl group of 1 to 8 carbon atoms;

or
the formula (III):

(III)



wherein each of R^{31} , R^{32} , R^{33} and R^{34} independently represents a hydrogen atom or an alkyl group of 1 to 8 carbon atoms.

13. The pressure sensitive recording material as defined in claim 11, wherein the bisphenol compound is contained in the mixture in an amount of 5 to 30 weight parts based on 100 weight parts of the vegetable oil.
14. The pressure sensitive recording material as defined in claim 11, wherein the vegetable oil is at least one selected from the group consisting of soybean oil, corn oil, rapeseed oil, cotton seed oil, sesame oil, peanut oil and sunflower oil.
15. The pressure sensitive recording material as defined in claim 11, wherein the developer comprises clay materials.

FIG. 1

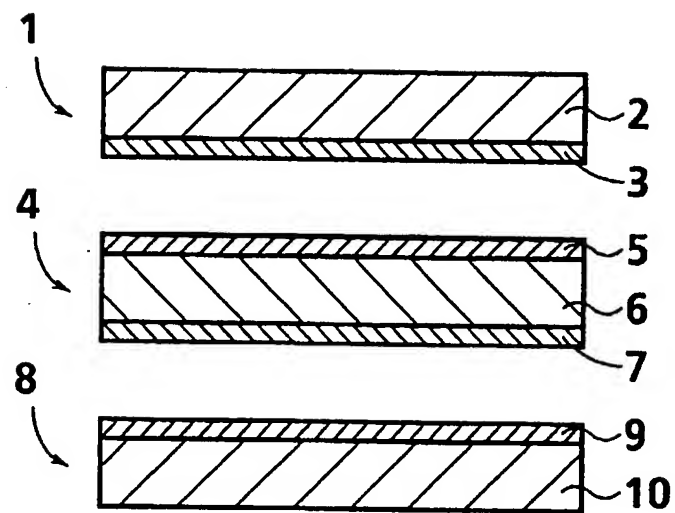


FIG. 2

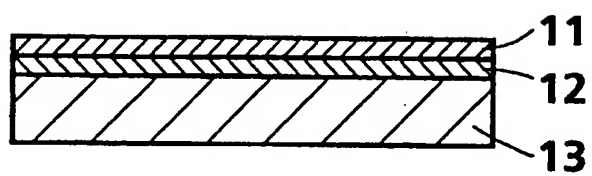
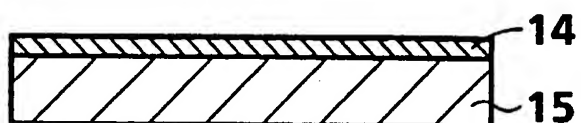
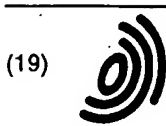


FIG. 3





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(54) **Recording material**

(57) A recording material contains both a microcapsule containing an electron-donating color former dissolved in a solvent and an electron-accepting developer. The electron-donating color former comprises Crystal Violet Lactone, and the solvent comprises a mixture of a

vegetable oil which has a fatty acid residue composition containing an oleic acid residue in the range of 10 to 60 weight % and a specific bisphenol compound, the bisphenol compound being contained in the mixture in an amount of 2 to 40 weight parts based on 100 weight parts of the vegetable oil.

EP 0 718 116 A3



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EUROPEAN SEARCH REPORT

Application Number
EP 95 30 9210

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
D,A	DATABASE WPI Week 7710 Derwent Publications Ltd., London, GB; AN 77-16908Y XP002004255 & JP-A-50 090 409 (FUJI PHOTO FILM) * abstract * ---	1	B41M5/28 B41M5/165
D,A, P	EP-A-0 629 511 (FUJI PHOTO FILM) * the whole document * & JP-A-06 340 169 ---	1	
D,A	EP-A-0 273 752 (FUJI PHOTO FILM) * the whole document * ---	1	
D,A	EP-A-0 247 816 (FUJI PHOTO FILM) * the whole document * ---	1	
			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
			B41M
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 30 May 1996	Examiner Heywood, C
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